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## On the thermodynamics of classical liquids

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### Abstract

A model is suggested for a classical liquid, based on local vibrations of molecular concentration.

In contrast with gases or solids, or even more complex quantal ensembles, the classical liquids exhibit no particular distinction. Gases are rarefied ensembles of molecules moving freely, solids are made of molecules vibrating around regular positions. In contrast, all what we know about classical liquids is a general and rather vague picture of an ensemble of molecules, moving around and interacting strongly. This is why the thermodynamics of classical liquids lagged behind other statistical ensembles. Though it is true, on one side, that such a thermodynamics would not be very telling, it is also true, however, that we still lack it, in fact.

Actually, a closer scrutiny of the classical liquids may provide nevertheless some elements which may be helpful in building up such a thermodynamics.

First, we note that the molecules in a classical liquid are more or less bound together, albeit in a loose way, because we need a definite amount of energy  $\varepsilon_0$  to take a molecule out of such a liquid. Therefore, we may assign a cohesion energy  $-\varepsilon_0 < 0$  to each molecule in a classical liquid. Next, the molecules in a liquid may assume a pretty dense energy levels in their movement, at least over a certain energy range. We may imagine that their energy depends on the local inter-particle spacing  $a$ , and write it as  $\varepsilon(a)$ . During the motion the parameter  $a$  changes by small amounts  $\delta a$  with respect to its equilibrium value, so that we may set up a series expansion

$$\varepsilon = -\varepsilon_0 + A(\delta a)^2 + \dots \quad (1)$$

for the molecule energy, where the first-order term is absent, as for equilibrium, and  $A$  is some expansion coefficient. The change  $\delta a$  represents certainly a vibration, and for a macroscopic occupation the vibration energy goes like  $\varepsilon_{vib} \sim n \sim (\delta a)^2$ , where  $n$  is a large quantal number of vibrations. We extend this number down to quantal levels too (because the quantal motion is in there!), and set up  $n = 0, 1, 2, \dots$ . The energy given by (1) becomes therefore

$$\varepsilon = -\varepsilon_0 + \varepsilon_1 n + \dots, \quad (2)$$

where  $\varepsilon_1$  is the separation between the energy levels. For large vibrations the higher-order terms in (1) are certainly important, as corresponding to anharmonic vibrations, so we restrict the running of number  $n$  to some cutoff  $n_c$ , corresponding to a cutoff energy  $\varepsilon_2 = \varepsilon_1 n_c$ , if we do not want to include explicitly the anharmonic corrections. This is the most simple particle spectrum of the

molecules in a classical liquid, corresponding to a harmonic oscillator with one degree of freedom, as given by equation (2).

Next we define sub-ensembles in the liquid, labelled by  $j$ , each containing a large number  $N_j$  of molecules, centered on some points  $\mathbf{r}_j$  in space and some numbers  $n_j$  in the energy spectrum, each consisting of a number of states  $G_j = \Delta \mathbf{r}_j \Delta n_j / b$ , where  $b$  is a characteristic volume. The parameter  $b$  is reminiscent of the van der Waals excluding volume, plays the role of a volume cutoff and accounts for the "impenetrability" of the classical molecules and their short-range correlations. We set then the classical entropy

$$S = \sum_j \ln G_j^{N_j} / N_j! = - \sum_j G_j \rho_j \ln(\rho_j / e) = -(1/b) \int d\mathbf{r} dn \cdot \rho \ln(\rho / e) , \quad (3)$$

and view  $\rho_j = N_j / G_j = b dN / d\mathbf{r} dn = \rho$  as the probability density of the  $j$ -th statistical sub-ensemble. We look, as usually, for the maximal value of the entropy given by (3) subjected to a given number of molecules

$$N = \sum_j G_j \rho_j = (1/b) \int d\mathbf{r} dn \cdot \rho , \quad (4)$$

and a given energy

$$E = -N\varepsilon_0 + \sum_j G_j \varepsilon_j \rho_j = -N\varepsilon_0 + (1/b) \int d\mathbf{r} dn \cdot \varepsilon \rho , \quad (5)$$

where  $\varepsilon_j = \varepsilon_1 n_j$ . The constrained entropy functional reads

$$S = -(1/b) \int d\mathbf{r} dn \cdot \rho \ln(\rho / e) + \alpha [N - (1/b) \int d\mathbf{r} dn \cdot \rho] + \beta [E + N\varepsilon_0 - (1/b) \int d\mathbf{r} dn \cdot \varepsilon \rho] , \quad (6)$$

and we get straightforwardly the Boltzmann distribution

$$\rho = e^{-\alpha - \beta \varepsilon} , \quad (7)$$

where  $\varepsilon = \varepsilon_1 n$ . In addition, we get by (6) the inverse of the temperature  $\beta = 1/T = \partial S / \partial E$ , the chemical potential  $\mu = \partial E / \partial N = -\alpha T - \varepsilon_0$  and the pressure  $p = -\partial E / \partial V$  given by

$$E = -N\varepsilon_0 - pV + \mu N + TS , \quad (8)$$

where  $V$  denotes the volume, *i.e.* the basic thermodynamics,  $dE = -pdV + TdS + \mu dN$  including.

The distribution given by (7) can also be written as

$$dN = (V/b) e^{\beta(\mu + \varepsilon_0)} e^{-\beta \varepsilon_1 n} dn . \quad (9)$$

Equation (4) gives then the number of molecules

$$N = \frac{VT}{b\varepsilon_1} e^{\beta(\mu + \varepsilon_0)} (1 - e^{-\beta \varepsilon_2}) \quad (10)$$

which determines the chemical potential

$$\mu = -\varepsilon_0 - T \ln [T(1 - e^{-\beta \varepsilon_2}) / b\varepsilon_1 n] , \quad (11)$$

where  $n = N/V$  is the molecular concentration. In deriving (10) use has been made of the cutoff energy  $\varepsilon_2$ . In addition,  $\varepsilon_2 \sim T \gg \varepsilon_1$  in order to ensure the thermal equilibrium. These inequalities establish a range of temperatures around  $\varepsilon_2$  over which the liquid behaves consistently

and classically. Under these circumstances, the chemical potential given by (11) is close to  $\mu \sim -\varepsilon_0 - T \ln[\varepsilon_2/b\varepsilon_1 n]$ , *i.e.* it acquires large, negative values.

Making use of the Boltzmann distribution (9) the energy given by (4) reads

$$E = -N\varepsilon_0 + NT - N\varepsilon_2/(e^{\beta\varepsilon_2} - 1) , \quad (12)$$

and the entropy given by (3) becomes

$$S = N \ln[T(1 - e^{-\beta\varepsilon_2})/b\varepsilon_1 n] - \beta N\varepsilon_2/(e^{\beta\varepsilon_2} - 1) + 2N . \quad (13)$$

The free energy is then readily obtained as

$$F = E - TS = -N\varepsilon_0 - NT - NT \ln[T(1 - e^{-\beta\varepsilon_2})/b\varepsilon_1 n] , \quad (14)$$

so the pressure is given by

$$p = -\partial F/\partial V = NT/V . \quad (15)$$

This is the equation of state for a classical gas, as expected (the dependence of  $\varepsilon_0$  on concentration is neglected). The only difference consists in its large values in comparison with those in an ideal classical gas, corresponding to the high concentrations in liquids. The latter is about  $10^3$  larger than in gases, so is the liquid pressure. This tremendous pressure is compensated by the change in the binding energy  $\varepsilon_0$ , which depends on  $a \sim (V/N)^{1/3}$ , and, of course, the external (atmospheric) pressure. This makes the liquid practically incompressible. It is worth noting that, rigorously speaking, the parameters  $\varepsilon_{0,1,2}$  also depend on the concentration.

The heat capacity per particle at constant volume is

$$c_V = T(\partial S/\partial T)_V = 1 - \varepsilon_2^2 e^{\beta\varepsilon_2}/(e^{\beta\varepsilon_2} - 1)^2 , \quad (16)$$

while the heat capacity per particle at constant pressure is  $c_p = T(\partial S/\partial T)_p = c_V + 1$ . The Gibbs potential is given by

$$\Phi = \mu N = -N\varepsilon_0 - NT \ln[T^2(1 - e^{-\beta\varepsilon_2})/b\varepsilon_1 p] , \quad (17)$$

and the volume

$$V = \partial \Phi/\partial p = -(N/T)\varepsilon_0'(p/T) + NT/p , \quad (18)$$

where we view  $\varepsilon_0$  as a function of concentration  $\varepsilon_0 = \varepsilon_0(n) = \varepsilon_0(p/T)$ . The coefficient of thermal expansion is given by

$$\alpha = (1/V)(\partial V/\partial T)_p = \frac{1}{T} + \frac{p}{T^3}\varepsilon_0'(p/T) + \frac{p^2}{T^4}\varepsilon_0''(p/T) \quad (19)$$

and acquires positive values. Simialrly, the compressibilities can also be calculated from (18).

Making use of Boltzmann distribution (7) we can calculate the fluctuations  $\delta n$  in the quantal number  $n$  in equation (2), and hence the fluctuations in molecular volume  $\delta v \sim \delta a \sim \delta n$ . We get

$$\langle n^2 \rangle / \langle n \rangle^2 = (1/bn) \frac{e^{\beta\varepsilon_2}}{e^{\beta\varepsilon_2} - 1 - \beta\varepsilon_2} \left[ 2 + \frac{\beta\varepsilon_2(1 - \beta\varepsilon_2)}{e^{\beta\varepsilon_2} - 1 - \beta\varepsilon_2} \right] , \quad (20)$$

and get  $\delta v/v \sim 1/\sqrt{bn}$  in the limit  $\beta\varepsilon_2 \rightarrow \infty$  and  $\delta v/v \sim 1/\sqrt{bn}(T/\varepsilon_2)$  in the limit  $\beta\varepsilon_2 \rightarrow 0$ , where  $n$  denotes the concentration.

As one can see, at high temperatures the fluctuations increase indefinitely, as expected, and the energy spectrum and the thermal equilibrium are gradually lost. The chemical potential given by (11) reduces in this case to  $-\varepsilon_0$ , which can be used to be compared with the chemical potential of the gas, for phase equilibrium and liquid-gas transition. The transition from liquid to gas can be described by forming free clusters made of new numbers  $n_j$  of liquids, preserving the conservation of molecules by  $N = \sum n_j \rho_j$ , and solving for equilibrium, and transition, from  $n_j = \infty$  to  $n_j = 1$ . This is the reverse process of condensation of gases.